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EXECUTIVE SUMMARY OF THE THESIS

Spatially resolved investigation of methane oxidation over Pd-based catalyst: effect of fuel composition and water concentration

TESI MAGISTRALE IN ENERGY ENGINEERING – INGEGNERIA ENERGETICA

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1. Introduction

The growing environmental awareness and the stringent limitations set by policymakers encourage the employment of cleaner fuel in the automotive sector [1]. In this scenario, natural gas and biomethane seem to be really promising.

The main component of natural gas is methane (CH_4), which is the hydrocarbon with the highest H/C ratio. Due to this, for the same distance travelled, a natural vehicle (NGV) is characterized by lower CO_2 emissions, which are one of the major contributors to global warming. Also, particular matter, NO_x and CO emitted are lower compared to the other fossil fuels powered engines. The aftertreatment section of a typical NGV consists of the so-called three-way catalytic converter (TWC), already installed in gasoline vehicles, which operate under close stoichiometric conditions. Unfortunately, at the typical temperatures of the NGV exhaust, methane is hard to be oxidized because of the high stability of the C-H bonds.

Some strategies are needed to avoid unburnt methane emissions: CH_4 has a GWP potential 32 times higher compared to CO_2 [2].

2. Objective of the study

In this work, the performances of a commercial Pd-Rh/ Al_2O_3 catalyst were tested in a wide range of conditions. Experiments were carried out varying the feed composition and the reaction temperature, in order to better understand the behaviour of the catalyst towards the conversion of methane. The focus of the experimental activity was on the measurement of concentration and temperature profiles, which were obtained by means of the spatially resolved sampling technique. Collected data allowed to investigate the effect of temperature, water poisoning and fuel-type on the activity of the Pd-based catalyst.

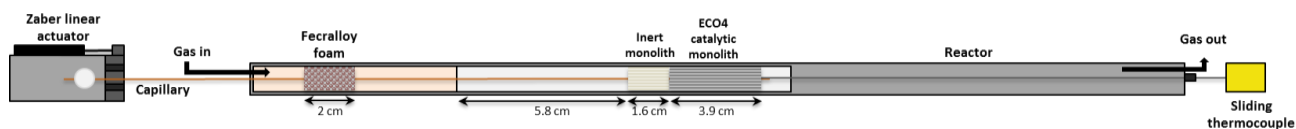


Figure 1 - Reactor loading configuration

3. Materials and methods

A commercial 400 CPSI Pd-Rh/Al₂O₃ honeycomb catalyst, 7.1 g/L loaded (Pd:Rh-39:1) promoted with Ce-Zr mixed oxides was tested in a stainless steel reactor (Figure 1). The catalyst sample employed during experiments is a 6x6 channels, 3.9 cm long honeycomb monolith. A 1.6 cm long inert cordierite monolith is inserted, immediately before the catalyst honeycomb, as a guide for the sampling capillary. Also, a 2 cm long Fecralloy foam is placed: thanks to its randomly porous structure it is able to enhance the axial mixing of the feed stream, to obtain a better reactants distribution.

The CH₄ abatement performance was evaluated through the acquisition of spatially resolved profiles of gas composition with a quartz capillary connected to micro-GC. Temperature profiles were also collected by means of a thermocouple inserted in the sliding capillary.

Prior to each experimental campaign, degreening and conditioning procedures had to be performed in order to remove impurities and stabilize catalytic performances of the sample.

The gas hourly space velocity (GHSV) was kept constant at 50000 h⁻¹ referred to the honeycomb volume.

Two sets of feed mixture composition (A and B) were investigated. The compositions are reported in Table 1: composition A is representative of the exhausts from a natural gas vehicle, while composition B was adopted to investigate the behaviour of CH₄ in the absence of other fuel components.

Table 1 – feed mixture compositions, A and B

$y_{i,A}$ [vol%]	0.15	0.1	0.6	0-10	0.46-1.02	10.7	Balance
$y_{i,B}$ [vol%]	0.325	0	0	0-10	0.46-1.02	10.7	Balance

Experiments were accomplished by varying the lambda, defined as the ratio between the actual air flow rate and the theoretical one required by the

stoichiometry for complete fuel oxidation in the engine.

The different λ values are obtained by changing the oxygen content in the feed mixture and adjusting the N₂ concentration to balance the total flow rate. Also, the effect of feed water has been investigated, keeping constant the total flow rate in the same way.

A technique developed in previous studies [3] was employed with the aim of maintaining CH₄ downstream conversion constant throughout the test, consisting in periodically switching the feed to strongly rich conditions ($\lambda = 0.98$, O₂ = 0.26 %) for a short period of time (30 s).

4. Experimental results

The experimental study was focused on the evaluation of temperature and reactants concentration profiles along the monolith by means of the spatially resolved sampling technique.

Two experimental campaigns have been performed, the first one by using a mixture of CH₄/CO/H₂, while the second one by running pure methane as fuel.

4.1. CH₄-CO-H₂ feed

First, a feed composition made of CH₄, CO and H₂ has been investigated, according to the classical composition of NGVs exhausts.

To investigate how temperature affects the methane conversion along the catalyst sample, tests at three oxygen content ($\lambda = 1.02, 0.9963, 0.99$) are performed at 450 and 400 °C.

Concentration and temperature profiles are reported in Figure 2, at 450 °C and 10 % water content.

While CO and H₂ conversion in the first oxidation zone are independent of λ , CH₄ conversion shows specific trends which vary a lot with the feed stoichiometry. At $\lambda = 0.9963$, it is possible to highlight two different trends in methane consumption perfectly matched by the profile of oxygen concentration. In the first section of the catalyst, a slower oxidation seems to be responsible

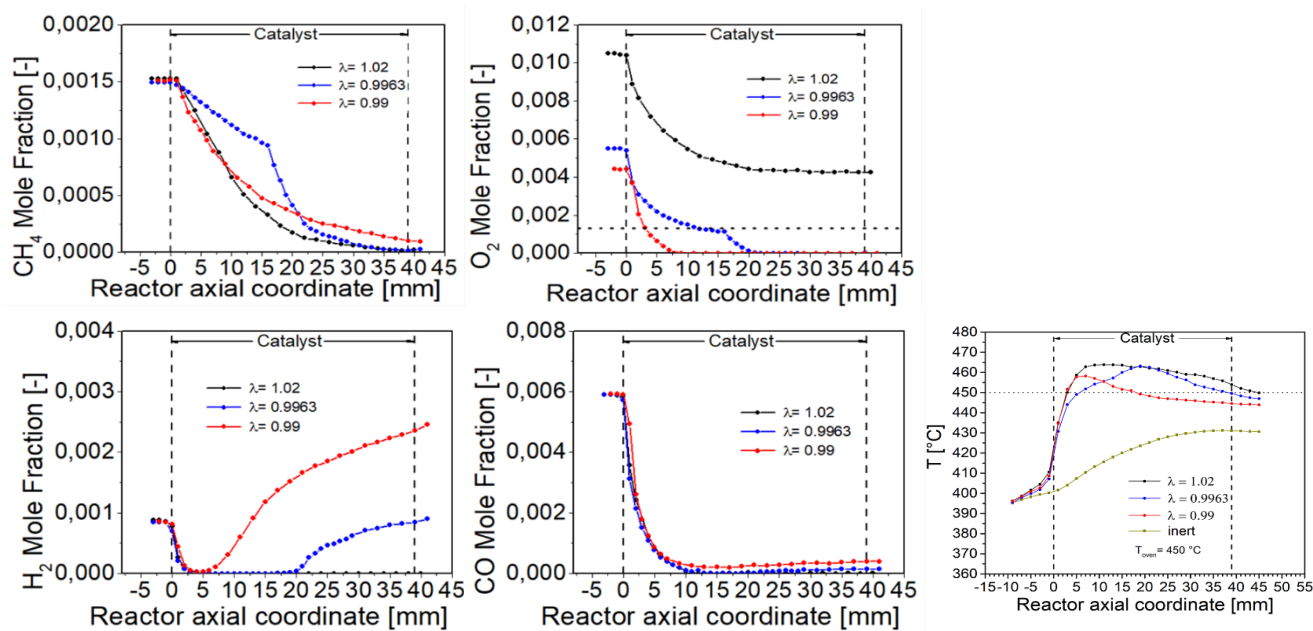


Figure 2 – Concentration profiles and temperature profiles throughout the monolith sample, at $T_{\text{oven}} = 450\text{ °C}$ and 10% H_2O , $\text{CH}_4\text{-CO-H}_2$ feed

for methane conversion. A sharp increment in the consumption rate is then identified.

This change in methane conversion rate occurs when an oxygen molar fraction equal to 0.0015 is reached. Downstream this section of the monolith, after O_2 has been completely consumed thanks to the boost of CH_4 consumption rate, steam reforming of methane continues until almost complete conversion.

Chin et al. [4] propose a correlation between the temperature and the O_2 partial pressure at which transition metallic Pd – Palladium oxide phase occurs. At $T = 450\text{ °C}$, it coincides with the O_2 concentration threshold at which methane conversion rate increases. Therefore, it is highly probable that the boost in methane conversion is related to a rearrangement of the Pd-based catalyst, which improves the oxygen mobility at the catalyst surface.

An alternative explanation may involve the activation of an “enhanced SR” as proposed by Wang et al. [5], that attributed this phenomenon to the desorption of carbonaceous species from ceria sites which normally hinder the rate of SR reaction. Correspondingly, the oxygen consumption is boosted by the oxidation of hydrogen and carbon monoxide, produced by the enhanced steam reforming, which are in fact observed only when O_2 is completely depleted.

At fully-rich mixture ($\lambda = 0.99$) conversion of methane occurs through steam reforming in a large part of the reactor. Less evidence in the production of CO is due to the WGS reaction occurring at the

same time and promoted by the high water concentration.

The same experiments, carried out at 400 °C are showed in Figure 3.

In line with previous results at higher temperature, no differences are visible in the oxidation of CO and H_2 when changing λ . CO and H_2 conversion rates are also independent of temperature, indicating that they are under external diffusion control.

On the other hand, all downstream methane conversions decrease from 450 °C to 400 °C because the CH_4 consumption reactions are kinetically limited by the temperature reduction. As a consequence in this new set of experimental data, SR does not occur at $\lambda = 0.9963$, since the oven temperature is not enough to sustain the complete consumption of oxygen. It is worth noting that the fully-rich mixture shows a sudden change in methane depletion rate, similar to that observed with $\lambda = 0.9963$ at 450 °C . The oxygen partial pressure at which methane conversion rate increases is, in this case, around 0.4 mbar. This result correlate satisfactorily well with the correspondence between temperature and critical value P_{O_2} reported for PdO/Pd transition in the previously mentioned article [4].

4.2. CH_4 feed

The second experimental campaign has been performed testing only methane as fuel. The CO and H_2 were replaced by the equivalent amount of

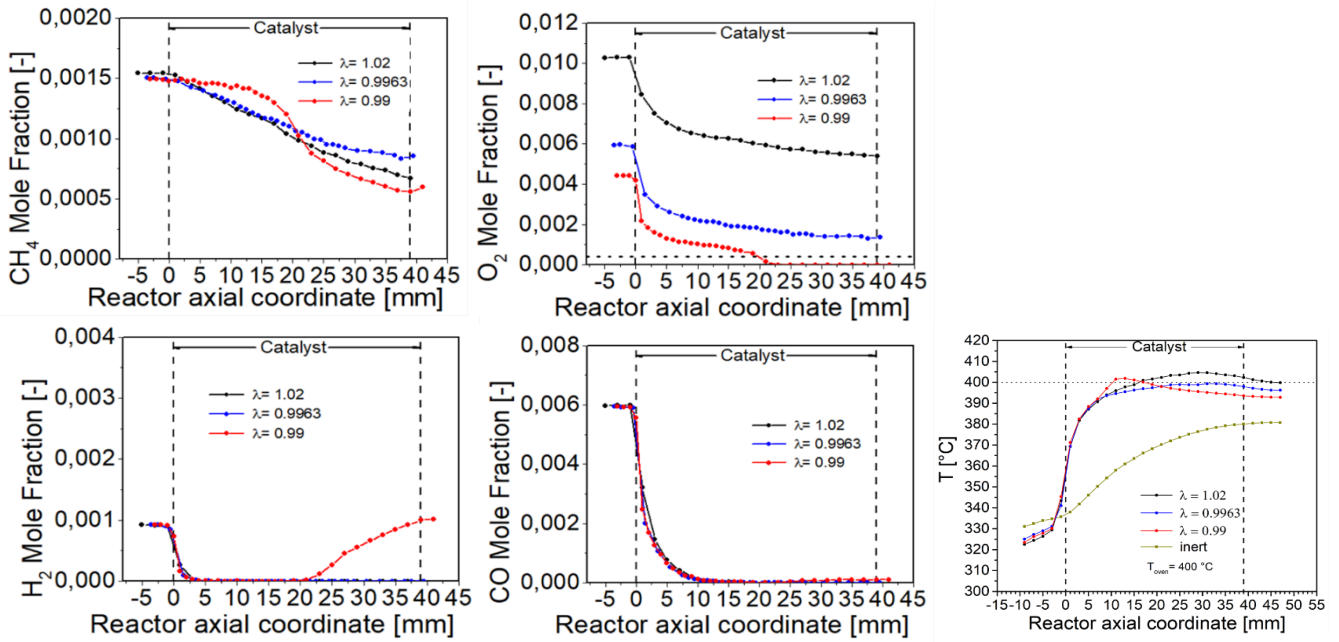


Figure 3 – Concentration profiles and temperature profiles throughout the monolith sample, at $T_{oven} = 400\text{ °C}$ and 10% H_2O , CH_4 - CO - H_2 feed

methane needed to keep constant the stoichiometry for O_2 consumption. The effect of water inhibition has been investigated by focusing for each of the representative lambda (1.02, 0.9963, 0.99) on two limit percentages of water co-feed (10 vol %, 0 vol %). Interesting results were obtained by feeding a $\lambda = 1.02$ mixture, at 10% of water. In good agreement with a recent work from Coney et al. [6], it has been observed that under lean wet conditions, the lower

the reaction temperature, the higher the inhibition of the catalyst for water poisoning. The concentration and temperature profiles, at both 450 °C and 400°C, are reported in Figure 4. At 450 °C, under dry feed practically all methane is removed, while, at 10% water content, a methane conversion equal to around 90% is reached. From the observation of both temperature and concentration profiles, it is evident that at 400 °C the effect of water inhibition is emphasized. Many researches agree that Pd catalysts supported on

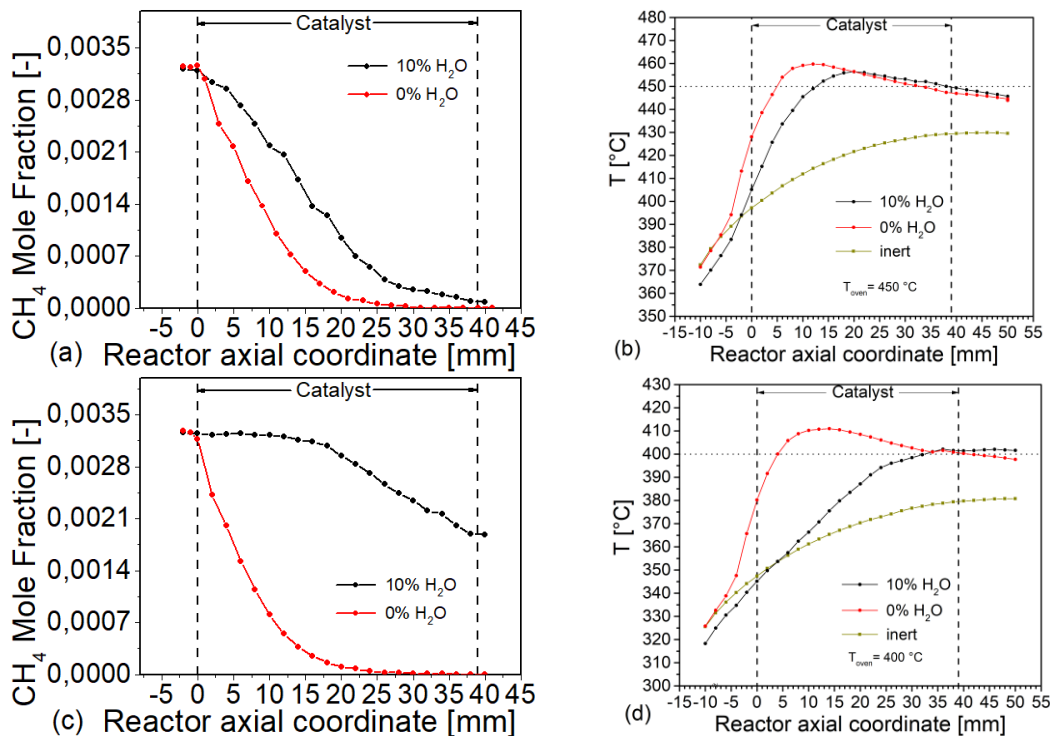


Figure 4 - Methane concentration as a function of axial position at 450 °C (a) and 400 °C (c). Gas temperature as a function of axial position at 450 °C (b) and 400 °C (d), CH_4 feed

alumina can form a $\text{Pd}(\text{OH})_x$ species, when H_2O is fed. These hydroxides are characterized by a slow water desorption rate, which is supposed to be the rate determining step. When a high amount of water is fed, H_2O is in competition with CH_4 to be adsorbed on the catalytic surface.

In agreement with this statement, in the temperature profile at 400°C (d), when the effects of water inhibition combines with that of decreasing temperature, it is possible to notice that the temperature increases very slowly along the reactor, thus resulting in a low rate of methane conversion. The methane oxidation (c) is highly inhibited for water poisoning and only a small quantity can be initially converted, thus resulting in a low reaction temperature. The lower the reaction temperature, the lower the rate of CH_4 conversion and so on.

In Figure 5 and Figure 6, the effects of water on the methane conversion, respectively at $\lambda = 0.9963$ and $\lambda = 0.99$, are illustrated. In both cases methane and oxygen consumptions exhibit an almost linear trend under dry feed. At $\lambda = 0.9963$, when 10% of water is co-fed, at around $x = 16$ mm the rate of methane conversion increases. At $\lambda = 0.99$ it is even more visible, when oxygen approaches a partial pressure around 3 mbar, the rate of methane conversion is boosted. This behaviour suggests that water may have an important role in the presence of this oxygen threshold.

When pure methane is used as fuel, the O_2 partial pressure at which the oxygen threshold occurs is different compared to the one found when CO and H_2 were co-fed. This behaviour seems not to be related to the reaction temperature, the heat released with the mixed fuel is higher due to the fast oxidation of hydrogen and carbon monoxide. By following the hypothesis of Chin et al., the oxygen threshold might be at a lower oxygen partial pressure, while in the experiments it is the opposite. For sure, further investigations are needed to fully comprehend this effect.

5. Conclusions

The first experimental campaign, performed by feeding a mixture of $\text{CH}_4\text{-CO-H}_2$ as fuel, showed that there is a critical partial pressure of oxygen below which methane conversion rate increased by one order of magnitude. This is supposed to be explained with the formation of a more active Pd/PdO state. Similar result has been obtained performing the same experiments at 400°C : the O_2 partial pressure threshold is still present but shifted towards a lower value.

This suggests that there is a relationship between the critical oxygen concentration and the reaction temperature, in complete agreement with literature.

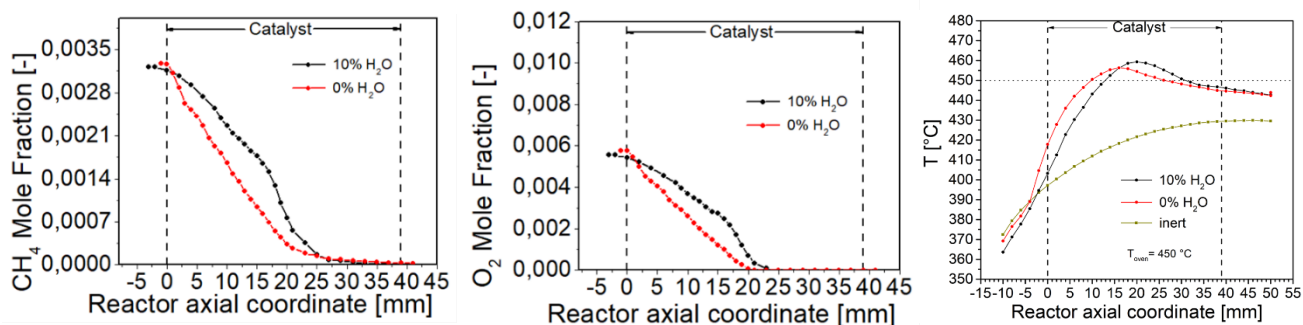


Figure 5 – CH_4 and O_2 concentration profiles and temperature profiles throughout the monolith sample, at $T_{\text{oven}} = 450^\circ\text{C}$ and $\lambda = 0.9963$, CH_4 feed

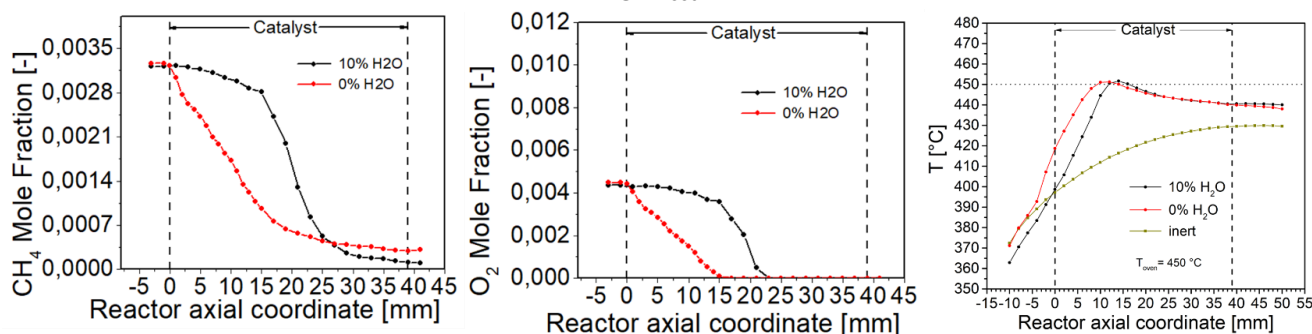


Figure 6 – CH_4 and O_2 concentration profiles and temperature profiles throughout the monolith sample, at $T_{\text{oven}} = 450^\circ\text{C}$ and $\lambda = 0.99$, CH_4 feed

Results also highlighted that under lean and slightly-rich conditions, where only oxidative reactions seem to occur, the water inhibition is great, while under rich conditions, a higher methane conversion is achieved when 10% of water is co-fed, due to the high contribution of SR. This provides evidence that when SR occurs there is a trade-off between the two effects.

The second experimental campaign results focused on water content effects, when only methane is fed as fuel. The inhibition of the catalyst activity resulted much higher at 400 °C than 450 °C, under lean conditions, due to a self-feeding effect: the temperature and the rate of methane oxidation influence each other negatively, lowering the performance of the catalyst. Under slightly-rich and rich conditions, under wet conditions, an oxygen threshold at which methane conversion is increased has been found. The O₂ partial pressure at which it occurs is a little bit higher than the one found when CO and H₂ were co-fed. Further studies are needed to fully understand this behaviour.

By focusing on the role of water, it could be stated that it has an impact on the presence of the O₂ threshold: with both fuels, no evidence of its occurrence has been found in dry tests.

Unfortunately, it is possible to identify the catalyst surface structure only by looking at concentration profiles, but no direct evidence of the actual state has been collected.

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